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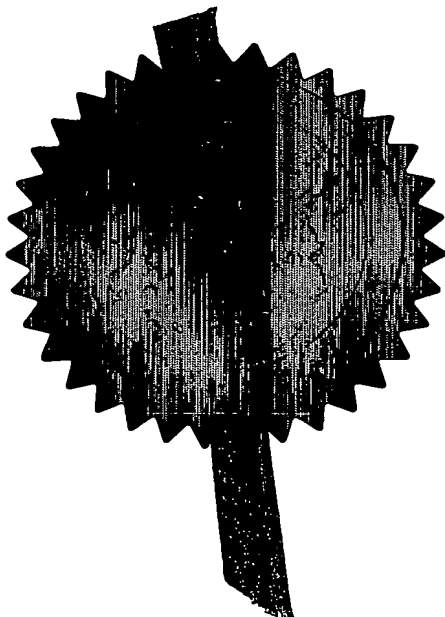
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SMC 60632/GB/P1

Patent application number
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28 NOV 2003

Full name, address and postcode of the or of
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Patents ADP number *(if you know it)*

07764137001 ✓

If the applicant is a corporate body, give the
country/state of its incorporation

GB

Title of the invention

Improvements in and Relating to Organic
Semiconducting Layers

Name of your agent *(if you have one)*

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Patents ADP number *(if you know it)*

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11.

I/We request the grant of a patent on the basis of this application.

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IMPROVEMENTS IN AND RELATING TO ORGANIC SEMICONDUCTING LAYERS

The present invention relates to an organic semiconducting layer formulation, a layer comprising the same, a process for preparing the formulation and layer and electronic devices comprising the same.

In recent years, there has been development of organic semiconducting materials in order to produce more versatile, lower cost electronic devices. Such materials find application in a wide range of devices or apparatus, including in organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), photodetectors, photovoltaic (PV) cells, and as organic photoconductors (OPCs) in electrophotographic devices, to name just a few. The organic semiconducting materials are typically present in the electronic device in the form of a thin layer, e.g. less than 1 micron thick.

It is desirable to improve both the charge mobility, μ , of organic semiconducting layers and to improve the layer integrity. It is also desirable to be able to deposit the layers by solution coating rather than by vapour deposition. One way to improve layer integrity has been to include the organic semiconducting component in an organic binder resin. However, whenever an organic semiconducting component is effectively "diluted" by a binder, a reduction of mobility is to be expected. Among other things, diluting an organic semiconductor by mixing with binders disrupts the molecular order in the semiconducting layer. Diluting an organic semiconducting component in the channel of an OFET for example is particularly problematic as any disruption of the orbital overlap between molecules in the immediate vicinity of the gate insulator (the first few molecular layers) is expected to reduce mobility. Electrons or holes then are forced to extend their path into the bulk of the organic semiconductor, which is undesirable.

Polyacene compounds are known in the prior art as organic semiconducting compounds and their use in FETs has been suggested (WO 03/016599, US 2003/0116755). It has also been suggested that a soluble polyacene may be mixed with a binder polymer.

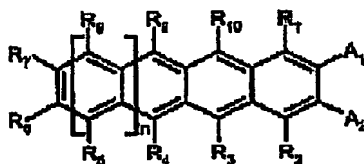
Certain low polarity binder resins are described in WO 02/45184 (Avecia) for use with organic semiconductors in FETs. However, a reduction in charge mobility is still expected when the semiconductor is diluted in the binder.

In WO 03/030278 (Phillips) there is shown a gradual reduction of FET mobility when a precursor polyacene (pentacene) is mixed with increasing amounts of binder. Furthermore, precursor polyacene requires chemical conversion following coating. This makes it possible for residual leaving groups to remain in the layer and complete conversion is difficult to achieve to the standards required for semiconductor purity. Control of the morphology is also difficult due to the conversion process. Accordingly, the prior art was unable to demonstrate high mobilities with a binder composition.

Among the objects of the present invention is to reduce or overcome the disadvantages in organic semiconducting layers described above.

According to the present invention there is provided an organic semiconducting layer formulation, which layer formulation comprises:

- a) a polyacene compound of formula 1



Formula 1

wherein each of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} , which may be the same or different, independently represents a hydrogen atom; an optionally substituted C_1 - C_{40} hydrocarbon group; an optionally substituted C_1 - C_{40} alkoxy group; an optionally substituted C_6 - C_{40} aryloxy group; an optionally substituted amino group; a hydroxy group; a halo group; or an optionally substituted silyl group; wherein R_6 and R_7 may be cross-bridged with each other to form a C_4 - C_{40} saturated or unsaturated ring, which saturated or unsaturated ring may be intervened by an oxygen atom, a sulphur atom or a group shown by formula: $-N(R_{11})-$ (wherein R_{11} is a hydrogen atom or a hydrocarbon group), or may optionally be substituted; each of A_1 and A_2 , which may be the same or different, independently represents a hydrogen atom; a halogen atom; an optionally substituted C_1 - C_{40} hydrocarbon group; an optionally substituted C_1 - C_{40} alkoxy group; an optionally substituted C_6 - C_{40} aryloxy group; an optionally substituted C_7 - C_{40} alkylaryloxy group; an optionally substituted C_2 - C_{40} alkoxycarbonyl group; an optionally substituted C_7 - C_{40} aryloxy carbonyl group; a cyano group ($-CN$); a carbamoyl group ($-C(=O)NH_2$); a haloformyl group ($-C(=O)-X$, wherein X represents a halogen atom); a formyl group ($-C(=O)-H$); an isocyano group; an isocyanate group; a thiocyanate group or a thioisocyanate group; wherein A_1 and A_2 may be cross-bridged with each other to form a ring shown by formula: $-C(=O)-B-C(=O)-$ (wherein B is an oxygen atom or a group shown by formula $-N(B_1)-$ (wherein B_1 is a hydrogen atom, a C_1 - C_{40} hydrocarbon group or a halogen atom)); and n is an integer not less than 1;

and

- b) an organic binder resin which has a permittivity, ϵ , at 1,000 Hz of 3.3 or less.

Surprisingly and beneficially, the inventors of the present invention have found that combining the specified soluble polyacene compound with the specified low permittivity

organic binder resin results in little or no reduction in charge mobility of the polyacene. At the same time, the semiconducting layer exhibits excellent film forming characteristics. Since the polyacenes of formula 1 are soluble they may also be deposited in a liquid form, e.g. from solution. For instance, a soluble polyacene may be dissolved, for example in polystyrene, and spin coated to form an OSC layer yielding a charge mobility as high as $0.3 \text{ cm}^2/\text{Vs}$. This result is particularly unexpected given that for such high mobilities the organic semiconducting layer is expected to require strong molecular ordering. We have found that even at 1:1 ratio of low permittivity binder/polyacene the mobility is about the same as that of the pure polyacene compound. The result produced by the present invention is therefore surprising for both a) maintaining the mobility despite potential disruption of molecular order, and b) maintaining mobility despite the expected increase of intermolecular distance. It is particularly surprising that the size of crystalline grains is reduced upon using a binder yet the mobility is high.

Once a formulation of high mobility is obtained by combining the polyacene with the specified binder, the resulting formulation leads to several advantages. Firstly, the formulation may be coated on a large area in a highly uniform manner. Without the use of binders the polyacenes cannot be spin coated on large areas as they do not result in uniform films. Spin and drop-casting may in some cases result in relatively high mobility but it is difficult to provide a film with a constant mobility over the entire substrate. Second, it is possible to control the properties of the formulation to adjust to printing processes, e.g. viscosity, solid content, surface tension. It is also anticipated that the binder fills in volume between crystalline grains otherwise being void, making the organic semiconducting layer less sensitive to air and moisture. For example, layers formed according to the present invention show very good stability in OFET devices in air.

The invention also provides an organic semiconducting layer which comprises the organic semiconducting layer formulation.

The invention further provides a process for preparing the organic semiconducting layer which comprises (i) depositing on a substrate a liquid layer of a mixture which comprises the polyacene compound, the organic binder resin or precursor thereof and optionally a solvent, and (ii) forming from the liquid layer a solid layer which is the organic semiconducting layer.

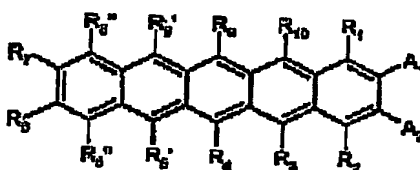
The invention additionally provides an electronic device comprising the said organic semiconducting layer. The electronic device may include, without limitation, an organic field effect transistor (OFET), organic light emitting diode (OLED), photodetector, or photovoltaic (PV) cell. For example, the active semiconductor channel between the drain and source in an OFET may comprise the layer of the invention. As another example, a charge (hole or electron) injection or transport layer in an OLED device may comprise the layer of the invention. The organic semiconducting layer may also find use

forming at least part of an organic photoconductor (OPC) in an electrophotographic device.

Certain polyacene compounds have been described in US 2003/0116755 and the methods disclosed therein for synthesising the polyacenes may be employed in the present invention in order to synthesise compounds of formula 1 above. Alternatively, other methods within the skill and knowledge of persons skilled in the art may be used to synthesise the compounds.

In one particular preferred embodiment, any one of the combinations of R_1 and R_2 , R_3 and R_{10} , R_4 and R_9 , R_5 and R_8 , R_6 and R_7 , and A_1 and A_2 are preferably the same substituents other than hydrogen, e.g. R_4 and R_9 may be the same substituent as each other.

Typically n is an integer from 1 to 3, preferably n is 2 (i.e. a pentacene derivative). The preferred pentacene derivative is represented generally by formula 1A below:

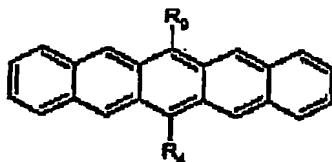


Formula 1A

Several preferred groups of pentacene derivatives according to formula 1A are represented below by groups 1-8.

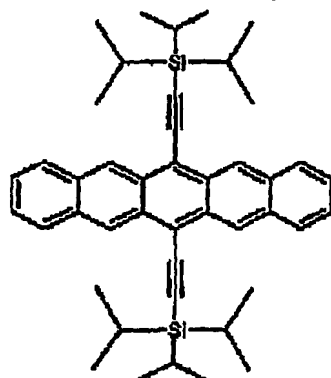
Group 1

General formula:

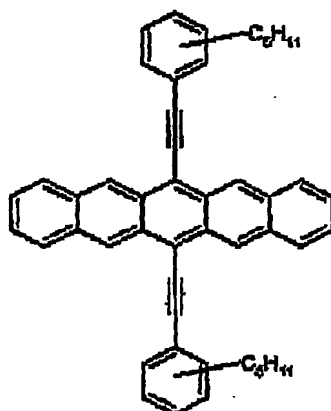


wherein R_4 and R_9 are other than hydrogen. In pentacene derivatives of group 1, R_4 and R_9 are preferably the same substituent as each other. Preferably, the groups R_4 and R_9 comprise optionally substituted C_1 - C_{40} hydrocarbon groups. More preferably, the groups R_4 and R_9 comprise optionally substituted unsaturated C_1 - C_{40} hydrocarbon groups, e.g. optionally substituted alkenyl, alkynyl, aryl etc. groups (alkynyl is a preferred group). Preferably, the R_4 and R_9 substituents are π -conjugated with the pentacene ring structure. In pentacene derivatives of group 1 the substituents other than R_4 and R_9 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

Examples of group 1 compounds are given below:



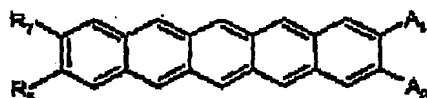
Group 1, example 1



Group 1, example 2

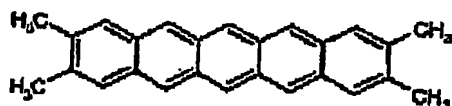
Group 2

General formula:



wherein R_6 , R_7 , A_1 and A_2 are other than hydrogen. In pentacene derivatives of group 2, R_6 and R_7 are preferably the same substituent as each other, and A_1 and A_2 are preferably the same substituent as each other. Preferably, R_6 , R_7 , A_1 and A_2 are the same substituent as each other. Preferably, the groups R_6 , R_7 , A_1 and A_2 comprise optionally substituted C_1 - C_{40} hydrocarbon groups. Further preferably, the groups R_6 , R_7 , A_1 and A_2 comprise optionally substituted C_1 - C_{10} hydrocarbon groups, e.g. methyl, ethyl, propyl, butyl, pentyl, etc. In pentacene derivatives of group 2 the substituents other than R_6 , R_7 , A_1 and A_2 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

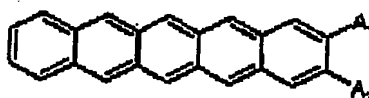
An example of a group 2 compound is given below:



Group 2, example

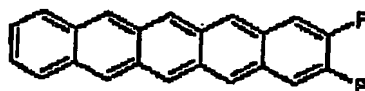
5 Group 3

General formula:



wherein A_1 and A_2 are other than hydrogen. In pentacene derivatives of group 3, A_1 and A_2 are preferably the same substituent as each other. Preferably, the groups A_1 and A_2 comprise optionally substituted C_1 - C_{40} hydrocarbon groups or halo. In pentacene derivatives of group 3 the substituents other than A_1 and A_2 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

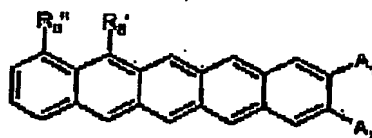
An example of a group 3 compound is given below:



Group 3 example

Group 4

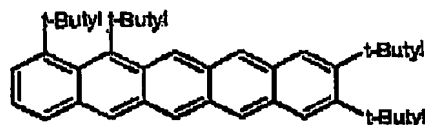
General formula:



wherein R_b' , R_b'' , A_1 and A_2 are other than hydrogen. In pentacene derivatives of group 4, R_b' and R_b'' are preferably the same substituent as each other, and A_1 and A_2 are preferably the same substituent as each other. Preferably, R_b' , R_b'' , A_1 and A_2 are the same substituent as each other. Preferably, the groups R_b' , R_b'' , A_1 and A_2 comprise optionally substituted C_1 - C_{40} hydrocarbon groups. Further preferably, the groups R_b' , R_b'' , A_1 and A_2 comprise optionally substituted C_1 - C_{10} hydrocarbon groups, e.g. methyl, ethyl, propyl, butyl, pentyl, etc. In pentacene derivatives of group 4 the substituents other than

R_3' , R_6'' , A_1 and A_2 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

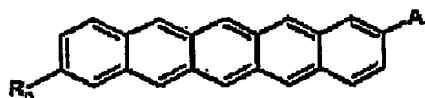
An example of a group 4 compound is given below:



Group 4, example

Group 5

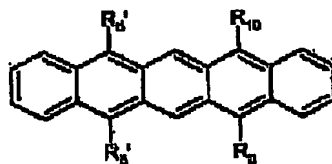
General formula:



wherein R_6 and A_1 are other than hydrogen. In pentacene derivatives of group 5, R_6 and A_1 are preferably the same substituent as each other. Preferably, the groups R_6 and A_1 comprise optionally substituted C_1 - C_{40} hydrocarbon groups. In pentacene derivatives of group 5 the substituents other than R_6 , R_7 , A_1 and A_2 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

Group 6

General formula:



wherein R_3 , R_{10} , R_6' and R_3' are other than hydrogen. In pentacene derivatives of group 6, R_3 and R_{10} are preferably the same substituent as each other, R_3' and R_6' are preferably the same substituent as each other. Preferably, R_3 , R_{10} , R_6' and R_3' are all the same substituent as each other. Preferably, the groups R_3 , R_{10} , R_6' and R_3' comprise optionally substituted C_1 - C_{40} hydrocarbon groups. In pentacene derivatives of group 6 the substituents other than R_6 , R_7 , A_1 and A_2 (i.e. R_1 , R_2 etc.) may be hydrogen or other substituents but typically may be hydrogen.

In groups 1-6 above, the optional substituents on the said C_1 - C_{40} hydrocarbon groups, preferably are selected from: silyl, sulpo, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halo, C_{1-4} alkyl, C_{6-12} aryl, C_{1-4} alkoxy, hydroxy and/or all chemically

possible combinations thereof. More preferable among these optional substituents are silyl and C_{6-12} aryl.

In this specification, the C_1-C_{40} hydrocarbon group may be a saturated or unsaturated acyclic group, or a saturated or unsaturated cyclic group. Unsaturated acyclic or cyclic groups are preferred, especially alkenyl and alkynyl groups. Where the C_1-C_{40} hydrocarbon group is acyclic, the group may be linear or branched. The C_1-C_{40} hydrocarbon group includes a C_1-C_{40} alkyl group, a C_2-C_{40} alkenyl group, a C_2-C_{40} alkynyl group, a C_3-C_{40} allyl group, a C_4-C_{40} alkylidienyl group, a C_4-C_{40} polyenyl group, a C_6-C_{40} aryl group, a C_6-C_{40} alkylaryl group, a C_6-C_{40} arylalkyl group, a C_4-C_{40} cycloalkyl group, a C_4-C_{40} cycloalkenyl group, and the like.

The C_1-C_{40} alkyl group, a C_2-C_{40} alkenyl group, a C_2-C_{40} alkynyl group, a C_3-C_{40} allyl group, a C_4-C_{40} alkylidienyl group, a C_4-C_{40} polyenyl group are preferably a C_1-C_{20} alkyl group, a C_2-C_{20} alkenyl group, a C_2-C_{20} alkynyl group, a C_3-C_{20} allyl group, a C_4-C_{20} alkylidienyl group and a C_4-C_{20} polyenyl group, respectively; and more preferably a C_1-C_{10} alkyl group, a C_2-C_{10} alkenyl group, a C_2-C_{10} alkynyl group, a C_3-C_{10} allyl group, a C_4-C_{10} alkylidienyl group and a C_4-C_{10} polyenyl group, respectively.

Examples of the alkyl group are, without limitation, methyl, ethyl, propyl, n-butyl, t-butyl, dodecanyl, trifluoromethyl, perfluoro-n-butyl, 2,2,2-trifluoroethyl, benzyl, 2-phenoxyethyl, etc. Examples of the aryl group are, without limitation, phenyl, 2-tolyl, 3-tolyl, 4-tolyl, naphthyl, biphenyl, 4-phenoxyphenyl, 4-fluorophenyl, 3-carbomethoxyphenyl, 4-carbomethoxyphenyl, etc. Examples of the alkoxy group are, without limitation, methoxy, ethoxy, 2-methoxyethoxy, t-butoxy, etc. Examples of the aryloxy group are, without limitation, phenoxy, naphthoxy, phenylphenoxy, 4-methylphenoxy, etc. Examples of the amino group are, without limitation, dimethylamino, methylamino, methyphenylamino, phenylamino, etc.

The silyl group, which may be optionally substituted, may be shown by formula: $-Si(R_{12})(R_{13})(R_{14})$ (wherein each of R_{12} , R_{13} and R_{14} , which may be the same or different, independently represents a C_1-C_{40} alkyl group which may optionally be substituted with a halogen atom; a C_6-C_{40} arylalkyl group which may optionally be substituted with a halogen atom; a C_1-C_{40} alkoxy group which may optionally be substituted with a halogen atom; or a C_6-C_{40} arylalkyloxy group which may optionally be substituted with a halogen atom).

A silyl group of formula $-Si(R_{12})(R_{13})(R_{14})$ as described above may also be a preferred optional substituent for the C_1-C_{40} hydrocarbon group.

Examples of the silyl group $-Si(R_{12})(R_{13})(R_{14})$ are, without limitation, trimethylsilyl, triethylsilyl, trimethoxysilyl, triethoxysilyl, diphenylmethylsilyl, triphenylsilyl, triphenoxysilyl, dimethylmethoxysilyl, dimethylphenoxyisilyl, methylmethoxyphenyl, etc.

R_6 and R_7 may be cross-bridged with each other to form a C_4-C_{40} saturated or unsaturated ring. The unsaturated ring may be an aromatic ring such as a benzene ring, etc. The ring formed by linking R_6 and R_7 together is preferably a 4-membered ring to a

16-membered ring, more preferably a 4-membered ring to a 12-membered ring. The ring may be an aromatic ring or an aliphatic ring. The ring may optionally be substituted with substituents such as a C₁-C₂₀ hydrocarbon group, a C₁-C₂₀ alkoxy group, a C₁-C₂₀ aryloxy group, an amino group, hydroxy group, a silyl group, etc. The saturated or unsaturated ring described above may be intervened by oxygen atom, sulphur atom or the group shown by formula -N(R₁₁)- (wherein R₁₁ is a hydrogen atom or a hydrocarbon group). Preferably R₁₁ is a hydrogen atom or a C₁-C₈ alkyl group, more preferably a hydrogen atom or a C₁-C₄ alkyl group.

In a preferred embodiment the semiconducting polyacene has a field effect mobility, μ , of more than 10^{-6} cm²V⁻¹s⁻¹, preferably of more than 10^{-4} cm²V⁻¹s⁻¹, more preferably of more than 10^{-3} cm²V⁻¹s⁻¹, still more preferably of more than 10^{-2} cm²V⁻¹s⁻¹ and most preferably of more than 10^{-1} cm²V⁻¹s⁻¹.

The organic binder resin, which is a polymer, may be referred to herein as the organic binder or simply the binder.

Preferred binders are materials of low permittivity. The organic binder preferably has a permittivity at 1,000 Hz of less than 3.0, more preferably 2.8 or less. Preferably the organic binder has a permittivity at 1,000 Hz greater than 1.7, especially a permittivity from 2.0 to 2.8.

An example of a suitable organic binder is polystyrene.

In one preferred embodiment, the organic binder is one in which at least 95%, more preferably at least 98% and especially all of the atoms are hydrogen, fluorine and carbon atoms.

It is preferred that the binder normally contains conjugated bonds especially conjugated double bonds and/or aromatic rings. The binder should preferably be capable of forming a film, more preferably a flexible film. Copolymers of styrene and alpha methyl styrene, for example copolymers of styrene, alpha methyl styrene and butadiene may suitably be used.

Binders of low permittivity of use in the present invention have few permanent dipoles which could otherwise lead to random fluctuations in molecular site energies. The permittivity (dielectric constant) can be determined by the ASTM D150 test method.

It is desirable that the permittivity of the binder has little dependence on frequency. This is typical of non-polar materials. Polymers and/or copolymers can be chosen as the binder by the permittivity of their substituent groups. A list of low polarity binders suitable for use in the present invention is given (without limiting to these examples) in Table 1 :

Table 1

Binder	typical low frequency permittivity ϵ
polystyrene	2.5
poly(α -methylstyrene)	2.6
poly(α -vinyl naphthalene)	2.6
poly(vinyltoluene)	2.6
polyethylene	2.2-2.3
cis-polybutadiene	2.0
polypropylene	2.2
polyisoprene	2.3
poly(4-methyl-1-pentene)	2.1
poly(tetrafluoroethylene)	2.1
poly(chlorotrifluoroethylene)	2.3-2.8
poly(2-methyl-1,3-butadiene)	2.4
poly(p-xylylene)	2.6
poly(α - α - α - α ' tetrafluoro-p-xylylene)	2.4
poly[1,1-(2-methyl propane)bis(4-phenyl)carbonate]	2.3
poly(cyclohexyl methacrylate)	2.5
poly(chlorostyrene)	2.6
poly(2,6-dimethyl-1,4-phenylene ether)	2.6
polyisobutylene	2.2
poly(vinyl cyclohexane)	2.2

Other polymers suitable as binders include poly(4-methylstyrene), poly(1,3-butadiene) or polyphenylene. Copolymers containing the repeat units of the above polymers are also suitable as binders. Copolymers offer the possibility of improving compatibility with the polyacene, modifying the morphology and/or the glass transition temperature of the final layer composition. It will be appreciated that in the above table certain materials are insoluble in commonly used solvents for preparing the layer. In these cases analogues can be used as copolymers. Some examples of copolymers are given in Table 2 (without limiting to these examples). Both random or block copolymers can be used. It is also possible to add some more polar monomer components as long as the overall composition remains low in polarity.

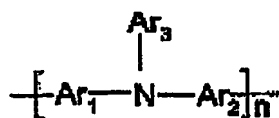
Table 2

Binder	typical low frequency permittivity (ϵ)
poly(ethylene/tetrafluoroethylene)	2.6
poly(ethylene/chlorotrifluoroethylene)	2.3
fluorinated ethylene/propylene copolymer	2-2.5
polystyrene-co- α -methylstyrene	2.5-2.6
ethylene/ethyl acrylate copolymer	2.8
poly(styrene/10%butadiene)	2.6
poly(styrene/15%butadiene)	2.6
poly(styrene/2,4 dimethylstyrene)	2.5

Other copolymers may include branched or non-branched polystyrene-block-polybutadiene, polystyrene-block(polyethylene-ran-butylene)-block-polystyrene, polystyrene-block-polybutadiene-block-polystyrene, polystyrene-(ethylene-propylene)-diblock-copolymers (e.g. KRATON®-G1701E, Shell), poly(propylene-co-ethylene) and poly(styrene-co-methylmethacrylate).

The organic binder itself may be a semiconductor, where it will be referred to herein as a semiconducting binder. The semiconducting binder is still a binder of low polarity as herein defined. The semiconducting binder preferably has a number average molecular weight (M_n) of at least 2000, preferably at least 3000, even more preferably at least 4000 and most preferably at least 5000. The semiconducting binder preferably has a charge carrier mobility, μ , of at least $10^{-8} \text{ cm}^2/\text{V.s.}$, more preferably at least $10^{-4} \text{ cm}^2/\text{V.s.}$

A preferred class of semiconducting binder has a formula 2



Formula 2

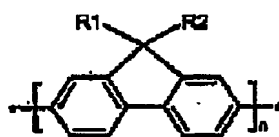
wherein Ar^1 , Ar^2 and Ar^3 , which may be the same or different, each represent, independently if in different repeat units, an optionally substituted aromatic group (mononuclear or polynuclear) and n is an integer of at least 5, preferably at least 10, more preferably at least 15 and most preferably at least 20. In the context of Ar^1 , Ar^2 and Ar^3 , a mononuclear aromatic group has only one aromatic ring, for example phenyl or phenylene. A polynuclear aromatic group has two or more aromatic rings which may be fused (for example naphthyl or naphthylene), individually covalently linked (for example biphenyl) and/or a combination of both fused and individually linked aromatic rings.

Preferably each Ar^1 , Ar^2 and Ar^3 is an aromatic group which is substantially conjugated over substantially the whole group.

Preferred classes of semiconducting binders are those containing substantially conjugated repeat units. The semiconducting polymer may be a homopolymer or copolymer (including a block-copolymer) of the general formula 3:

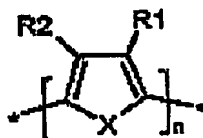


where A, B,...,Z each represent a monomer unit and (c), (d),...(z) each represent the fraction of the respective monomer unit in the polymer, i.e. each (c), (d),...(z) is a value from 0 to 1 and the total of (c) + (d) +...+ (z) = 1. Examples of monomer units A, B,...,Z include units of formula 2 and formulae 4 - 9 given below.



Formula 4

where R1 and R2 may be independently H; optionally substituted alkyl; alkoxy; thioalkyl; acyl; optionally substituted aryl; a fluorine atom; a cyano group; a nitro group; an optionally substituted secondary or tertiary alkylamine or arylamine $-N(R_a)(R_b)$, where R_a and R_b may each be independently represented by H, alkyl, substituted alkyl, aryl, substituted aryl, alkoxy or polyalkoxy groups; or other substituent and - is any terminal or end capping group including hydrogen. The alkyl and aryl groups may be optionally fluorinated;



Formula 5

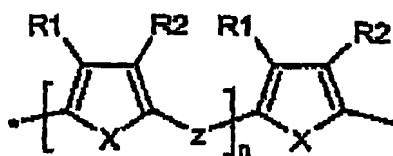
In which X may be Se, Te or preferably O, S or $-N(R)-$, where R represents H, alkyl, substituted alkyl, aryl, or substituted aryl; R1 and R2 are as for formula 4. The alkyl and aryl groups may be optionally fluorinated;

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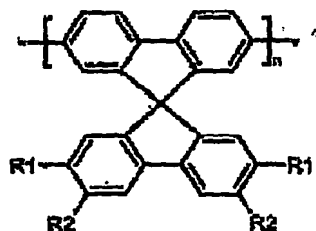
Formula 6

5 In which X, R1 and R2 are as for formula 4;



Formula 7

10 In which X is as for formula 4; R1, R2 are as for formula 4; and Z represents -
C(T₁)=C(T₂)-, -C≡C-, -N(R')-, -N=N-, (R')=N-, -N=C(R')-, T₁ and T₂ independently
15 represent -H, Cl, F, -C≡N or a lower alkyl, R' represents -H, alkyl, substituted alkyl, aryl,
or substituted aryl. The alkyl and aryl groups may also be optionally fluorinated ;



Formula 8

20 where R1 and R2 are as for formula 4. The alkyl and aryl groups may be optionally
fluorinated



Formula 9

where R1-R4 may be independently selected from the same list of groups as for R1 and R2 in formula 4;

In the case of a block-copolymer, each monomer A, B,...Z may be a conjugated oligomer or polymer comprising a number, for example 2 to 50, of the units of formulae 4-9. The semiconducting binder preferably includes arylamine, fluorene, thiophene, spiro bifluorene and/or optionally substituted aryl (e.g. phenylene) groups, more preferably arylamine, still more preferably triarylamine. The aforementioned groups may be linked by further conjugating groups e.g. vinylene. Additionally preferably the semiconducting binder comprises a polymer (either a homo-polymer or copolymer, including block-copolymer) containing one or more of the aforementioned arylamines, fluorene, thiophene and/or optionally substituted aryl groups. A preferred semiconducting binder comprises a homo-polymer or copolymer (including block-copolymer) containing arylamine (preferably triarylamine) and/or fluorene units. Another preferred semiconducting binder comprises a homo-polymer or co-polymer (including block-copolymer) containing fluorene and/or thiophene units.

The semiconducting binder may also contain carbazole, stilbene repeat units. For example polyvinylcarbazole or polystilbene polymers, copolymers may be used. The semiconducting binder may optionally contain polyacene segments (e.g. repeat units as formula 1 above) to improve compatibility with the soluble polyacene molecules.

For application of the semiconducting layer of the invention in p-channel FETs, it is desirable that the binder should have a higher ionisation potential than the polyacene semiconductor, otherwise the binder may form hole traps. In n-channel materials the binder should have lower electron affinity than the n-type semiconductor to avoid electron trapping.

The formulation according to the invention may be prepared by a process which comprises first mixing both the polyacene compound and the organic binder, preferably the mixing comprises mixing the two components together in a solvent. The solvent may be a single solvent or the polyacene compound and the organic binder may each be dissolved in a separate solvent followed by mixing the two resultant solutions to mix the compounds. The solvent(s) containing the polyacene compound and the organic binder may then be applied to a substrate. The solvent(s) may be evaporated to form the layer of the invention.

The binder may be formed *in situ* by mixing or dissolving the polyacene in a precursor of the binder, for example a liquid monomer, oligomer or crosslinkable polymer, optionally in the presence of a solvent, and depositing the mixture or solution, for example by dipping, spraying, painting or printing it, on a substrate to form a liquid layer and then curing the liquid monomer, oligomer or crosslinkable polymer, for example by exposure to radiation, heat or electron beams, to produce a solid layer.

If a preformed binder is used it may be dissolved together with the polyacene in a suitable solvent, and the solution deposited for example by dipping, spraying, painting or printing it on a substrate to form a liquid layer and then removing the solvent to leave a solid layer. Suitable solvents are chosen from those classes which are a good solvent for both the binder and polyacene, and which upon evaporation from the solution blend give a coherent defect free layer. Suitable solvents for the binder or polyacene can be determined by preparing a contour diagram for the material as described in ASTM Method D 3132 at the concentration at which the mixture will be employed. The material is added to a wide variety of solvents as described in the ASTM method. Examples of organic solvents which may be considered are: CH_2Cl_2 , CHCl_3 , monochlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, n-butyl acetate, dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetralin, decalin and/or mixtures thereof. After the appropriate mixing and ageing, solutions are evaluated as one of the following categories: complete solution, borderline solution or insoluble. The contour line is drawn to outline the solubility parameter-hydrogen bonding limits dividing solubility and insolubility. 'Complete' solvents falling within the solubility area can be chosen from literature values such as published in "Crowley, J.D., Teague, G.S. Jr and Lowe, J.W. Jr., Journal of Paint Technology, 38, No 496, 296 (1966)". Solvent blends may also be used and can be identified as described in "Solvents, W.H.Ellis, Federation of Societies for Coatings Technology, p9-10, 1986". Such a procedure may lead to a blend of 'non' solvents that will dissolve both the binder and polyacene, although it is desirable to have at least one true solvent in a blend.

The proportions of the binder to the polyacene in the layer according to the present invention are preferably 20:1 to 1:20, more preferably 10:1 to 1:10 and especially 5:1 to 1:5. Surprisingly and beneficially, dilution of the polyacene in the binder has been found to have little or no effect on the charge mobility, in contrast to what would have been expected from the prior art.

It is desirable to generate small structures in modern microelectronics to reduce cost (more devices/unit area), and power consumption. Patterning of the layer of the invention may be carried out by photolithography or electron beam lithography.

Liquid coating of organic electronic devices such as field effect transistors is more desirable than vacuum deposition techniques. The polyacene and binder mixtures of the present invention enable the use of a number of liquid coating techniques. The organic semiconductor layer may be incorporated into the final device structure by, for example and without limitation, dip coating, spin coating, ink jet printing, letter-press printing, screen printing, doctor blade coating, roller printing, reverse-roller printing, offset

lithography printing, flexographic printing, web printing, spray coating, brush coating or pad printing.

Selected polyacene and binder compositions of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

In order to be applied by Ink jet printing or microdispensing, polyacene and binder compositions must first be dissolved in a suitable solvent. Solvents must fulfil the requirements stated above and must not have any detrimental effect on the chosen print head. Additionally solvents should have boiling points $>100^{\circ}\text{C}$, more preferably $>150^{\circ}\text{C}$ in order to prevent operability problems caused by the solution drying out inside the print head. Suitable solvents include substituted and non-substituted xylene derivatives, di- C_{1-2} alkyl formamide, substituted and non-substituted anisoles and other phenol-ether derivatives, substituted heterocycles such as substituted pyridines, pyrazines, pyrimidines, pyrrolidones, substituted and non-substituted N,N -di- C_{1-2} -alkylanilines and other fluorinated or chlorinated aromatics. The use of the binder in the present invention also allows the viscosity of the coating solution to be tuned to meet the requirements of the particular print head.

The semiconducting layer of the present invention is typically at most 1 micron ($=1\mu\text{m}$) thick, although it may be thicker if required. The exact thickness of the layer will depend, for example, upon the requirements of the electronic device in which the layer is used. For use in an OFET or OLED, the layer thickness may typically be 500 nm or less.

In the semiconducting layer of the present invention there may be used two or more different polyacene compounds of formula 1. Additionally or alternatively, in the semiconducting layer there may be used two or more organic binder resins of the present invention.

As mentioned above, the invention further provides a process for preparing the organic semiconducting layer which comprises (i) depositing on a substrate a liquid layer of a mixture which comprises the polyacene compound, the organic binder resin or precursor thereof and optionally a solvent, and (ii) forming from the liquid layer a solid layer which is the organic semiconducting layer.

In the process, the solid layer may be formed by evaporation of the solvent and/or by reacting the binder resin precursor (if present) to form the binder resin *in situ*. The substrate may include any underlying layer, electrode or separate substrate such as silicon wafer or polymer for example.

The present invention also provides the use of the semiconducting formulation or layer in an electronic device. The formulation may be used as a high mobility semiconducting material in various devices and apparatus. The formulation may be used, for example, in the form of a semiconducting layer or film. Accordingly, in another aspect, the present invention provides a semiconducting layer for use in an electronic device, the layer comprising the formulation according to the invention. The layer or film may be less than about thirty microns. For various electronic device applications, the thickness may be less than about one micron thick. The layer may be deposited, e.g. on a part of an electronic device, by any of the aforementioned solution coating or printing techniques.

The formulation may be used, e.g. as a layer or film, in a field effect transistor (FET) e.g. as the semiconducting channel, organic light emitting diode (OLED) e.g. as a hole or electron injection or transport layer or electroluminescent layer, photodetector, chemical detector, photovoltaic cell (PVs), capacitor and the like. The formulation may also be used in electrophotographic (EP) apparatus, e.g. in the organic photoconductor. The formulation is preferably solution coated to form a layer or film in the aforementioned devices or apparatus to provide advantages in cost and versatility of manufacture. The improved charge carrier mobility of the formulation of the present invention enables such devices or apparatus to operate faster and/or more efficiently.

Some definitions and explanations of terms used herein are now given.

When in the formulae herein there is a list of labels (e.g. R_1 , R_2 etc.) or indices (e.g. n) which are said to represent a list of groups or numerical values, and these are said to be "independent in each case" this indicates each label and/or index can represent any of those groups listed independently from each other, independently within each repeat unit, independently within each Formula and/or independently on each group which is substituted as appropriate. Thus, in each of these instances, many different groups might be represented by a single label (e.g. R_0).

The terms 'substituent', 'substituted', 'optional substituent' and/or 'optionally substituted' as used herein (unless followed by a list of other substituents) signifies at least one of the following groups (or substitution by these groups): silyl, sulpho, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halo, C_{1-4} alkyl, C_{6-12} aryl, C_{1-4} alkoxy, hydroxy and/or combinations thereof. These optional groups may comprise all chemically possible combinations in the same group and/or a plurality (preferably two) of the aforementioned groups (e.g. amino and sulphonyl if directly attached to each other represent a sulphamoyl radical). Preferred optional substituents comprise: C_{1-4} alkyl; methoxy and/or ethoxy (any of these optionally substituted by at least one halo); amino (optionally substituted by at least one methyl and/or ethyl); and/or halo.

The term 'hydrocarbon group', 'hydrocarbyl' or the like may be used herein interchangeably. A hydrocarbon group may be optionally substituted. A hydrocarbon

group may also contain at least one of the following heteroatom containing moieties: oxy, thio, sulphinyl, sulphonyl, amino, imino, nitrilo and/or combinations thereof.

The terms 'alkyl', 'aryl', etc. as used herein may be readily replaced, where appropriate, by terms denoting a different degree of valence e.g. multivalent species (e.g. alkylene, arylene, etc.).

The term 'halo' as used herein signifies fluoro, chloro, bromo and iodo.

Unless the context clearly indicates otherwise, a group herein which comprises a chain of three or more carbon atoms signifies a group in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings).

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components.

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

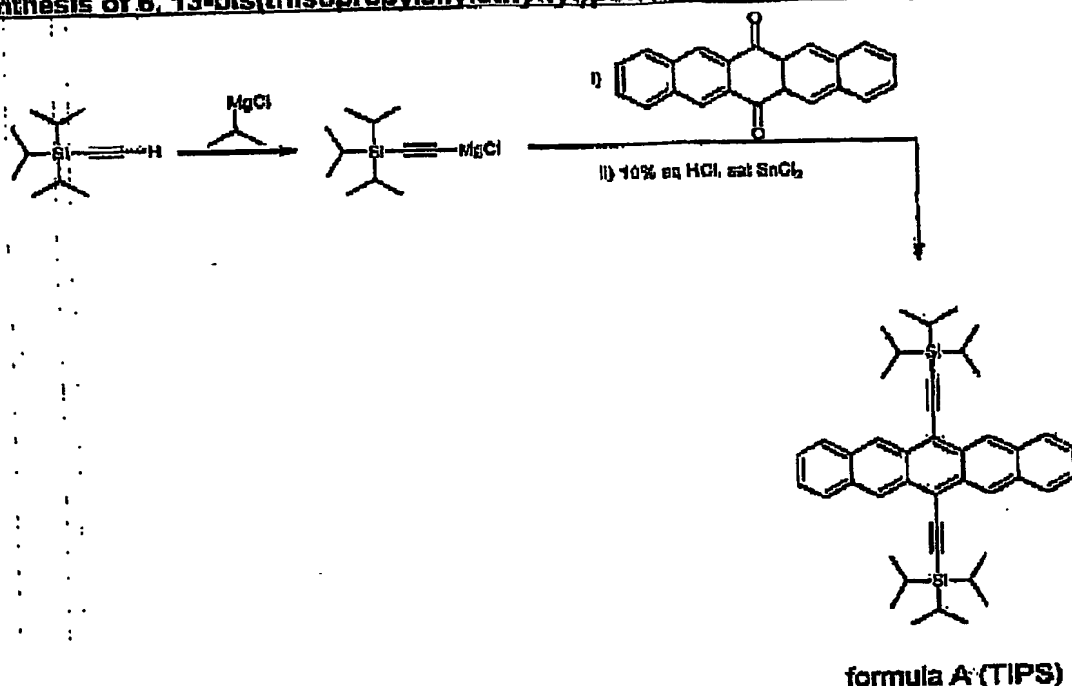
It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

The invention will now be described in more detail by reference to the following examples, which are illustrative only and do not limit the scope of the invention.

Examples

Synthesis of semiconductors

Synthesis of 6, 13-bis(trisopropylsilyl)ethynyl)pentacene - formula A (TIPS)



To a flame-dried flask fitted with mechanical stirrer, nitrogen inlet and outlet, condenser and sub-seal was added isopropylmagnesium chloride (2M in THF (10 molar equivalents based on 6, 13-pentacenequinone)). This solution was cooled using a cold-water bath to act as a cold trap to absorb any exotherm during the trisopropylsilyl acetylene addition. Trisopropylsilyl acetylene (10.1 molar equivalents based on 6, 13-pentacenequinone) was added to the reaction flask drop-wise over 30 minutes followed by the addition of THF (10ml for every 10mmol of TIPS acetylene). The cold-water bath was removed and then this solution was heated at 60 °C for 20 minutes. The flask was then allowed to cool to room temperature. 6, 13-Pentacenequinone (1 molar equivalent) was added to the Grignard reagent and the resulting cloudy suspension was heated at 60 °C until the reaction was deemed complete according to HPLC, this may take up to 3 hours. The flask was allowed to cool to room temperature. A solution of 10% aqueous HCl saturated with tin (II) chloride was added cautiously to the brown / red reaction solution until the solution no longer exothermed on addition. (It is noted that as the tin (II) chloride solution was added, the reaction solution turned from brown / red to a deep blue colour). The resulting solution was heated at 60 °C for 30 minutes before cooling to room temperature.

This crude mixture was worked up using water / DCM drying the organic phase over MgSO_4 , before filtering and concentrating under vacuum to give a blue / black solid. Purification by column chromatography (silica gel, 5% DCM in hexane) followed by recrystallisation from acetone yielded the title compound as dark blue plates.

Determination of the Field Effect Mobility

The field effect mobility of the materials was tested using the techniques described by Holland et al, J. Appl. Phys. Vol.75, p.7954 (1994).

In the following examples a test field effect transistor was manufactured by using a PEN substrate upon which were patterned Pt/Pd source and drain electrodes by standard techniques, e.g. shadow masking. Semiconductor formulations were made using TIPS (formula A above) blended with an inert binder resin (poly(alpha-methylstyrene)). The semiconductor formulation was dissolved one part into 99 parts of toluene, and spin coated onto the substrate at 600 rpm for 18s. To ensure complete drying the sample was placed in an oven for 20 minutes at 100 °C. For comparison films of purely TIPS material were coated by spin coating. These were then dried in an oven for 20 min at 100 °C. The insulator material (Cytop 107M, Asahi glass) was mixed 3 parts to 2 parts of perfluorosolvent (FC75, Acros cat. no. 12380) and then spin-coated onto the semiconductor giving a thickness typically of approximately 1 μm . The sample was placed once more in an oven at 100 °C to evaporate solvent from the insulator. A gold gate contact was defined over the device channel area by evaporation through a shadow mask. To determine the capacitance of the insulator layer a number of devices were prepared which consisted of a non-patterned Pt/Pd base layer, an insulator layer prepared in the same way as that on the FET device, and a top electrode of known geometry. The capacitance was measured using a hand-held multimeter, connected to the metal either side of the insulator. Other defining parameters of the transistor are the length of the drain and source electrodes facing each other ($W=30 \text{ mm}$) and their distance from each other ($L=130 \mu\text{m}$).

The voltages applied to the transistor are relative to the potential of the source electrode. In the case of a p type gate material, when a negative potential is applied to the gate, positive charge carriers (holes) are accumulated in the semiconductor on the other side of the gate dielectric. (For an n channel FET, positive voltages are applied). This is called the accumulation mode. The capacitance/area of the gate dielectric C_i determines the amount of the charge thus induced. When a negative potential V_{gs} is applied to the drain, the accumulated carriers yield a source-drain current I_{DS} which depends primarily on the density of accumulated carriers and, importantly, their mobility in the source-drain channel. Geometric factors such as the drain and source electrode configuration, size and distance also affect the current. Typically a range of gate and

drain voltages are scanned during the study of the device. The source-drain current is described by equation 1.

$$I_{DS} = \frac{\mu WC_1}{L} \left((V_G - V_0) V_{DS} - \frac{V_{DS}^2}{2} \right) + I_n, \quad \text{eq.1}$$

where V_0 is an offset voltage and I_n is an ohmic current independent of the gate voltage and is due to the finite conductivity of the material. The other parameters have been described above.

For the electrical measurements the transistor sample was mounted in a sample holder. Microprobe connections were made to the gate, drain and source electrodes using Karl Suss PH100 miniature probe-heads. These were linked to a Hewlett-Packard 4156B parameter analyser. The drain voltage was set to -20 V and the gate voltage was scanned from +20 to -60V and back to +20V in 1 V steps. In accumulation, when $|V_G| > |V_{DS}|$ the source-drain current varies linearly with V_G . Thus the field effect mobility can be calculated from the gradient (S) of I_{DS} vs. V_G given by equation 2.

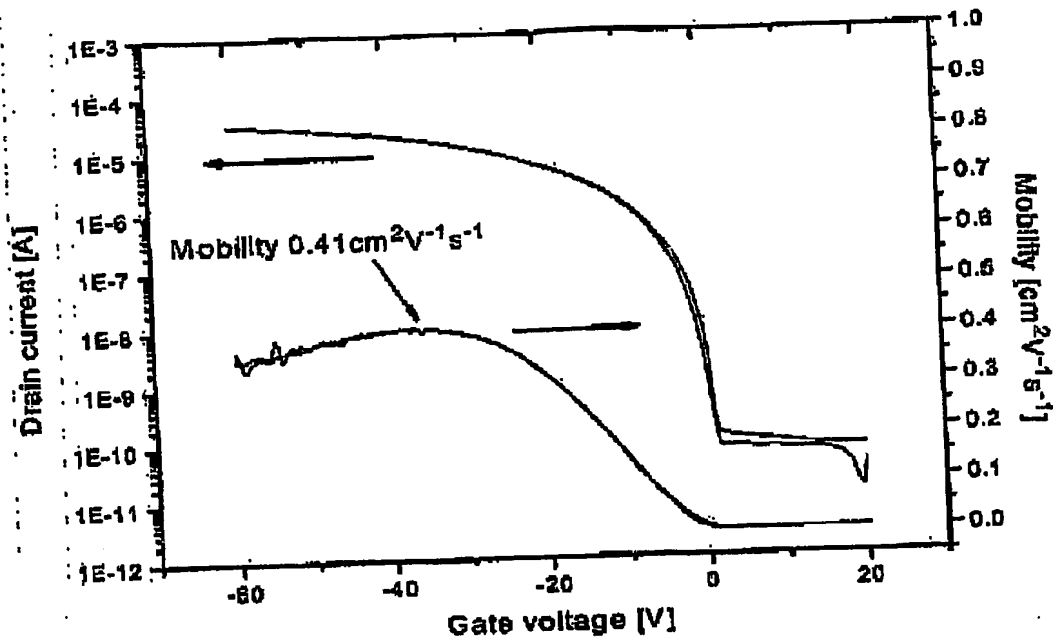
$$S = \frac{\mu WC_1 V_{DS}}{L} \quad \text{eq. 2.}$$

All field effect mobilities quoted below were calculated from this regime (unless stated otherwise). Where the field effect mobility varied with gate voltage, the value was taken as the highest level reached in the regime where $|V_G| > |V_{DS}|$ in accumulation mode. The values quoted in table 3 are an average taken over several devices (fabricated on the same substrate), the sample size is also quoted in table 3. An example of the current-voltage and mobility-voltage characteristics for example 1 is shown in figure 1. The forward and reverse scans illustrate the low hysteresis of the device.

Table 3 : results of the formulations tested

Example number	Organic semiconducting material (OSC)	Binder	OSC : binder ratio (wtwt)	OSC coating method	Mobility [cm^2/Vs]	Sample size
1	Formula A	p- α MS	50:50	Spin coat	0.433	9
2	Formula A	p- α MS	75:25	Spin coat	0.321	7
3	Formula A	p- α MS	90:10	Spin coat	0.327	6
4	Formula A	p- α MS	95:5	Spin coat	0.244	8
5 (comparative)	Formula A	-	100	Spin coat	0.138	6

p- α MS = Poly(alpha-methylstyrene), Aldrich Cat no. 19,184-1.



5 Figure 1 :Current voltage characteristics of a transistor fabricated using semiconductor formulation in example 1 (drain source voltage $-5V$, note drain current has been multiplied by -1 to display correctly on log scale)

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